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Full Paper

Deposition of platinum-group metals in sediment and water bodies along the coastal belt of Ghana

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Abstract: Water and sediment samples from seven water bodies along the coastal belt of Ghana were assessed for the deposition of platinum-group metals (PGM), i.e. platinum, palladium and rhodium. Source analysis of the results indicated probable anthropogenic origins which had a strong linkage to automobile and marine vessel emissions. In the sediment samples, pollution indicators revealed that all the seven water bodies along the coast had elevated levels of PGM above the background values. Significant correlation between the metals indicated a common anthropogenic origin of the PGM. Rhodium metal measured at Pra River estuary demonstrated opposite correlation with PGM to the other six sampling sites, which indicated another source other than automobile and marine vessel emissions of rhodium.

Keywords: platinum-group metals deposition, metal pollution, coastal belt of Ghana

INTRODUCTION

In recent years, environmental analyses have revealed the presence of elevated levels of platinum-group metals (PGM) in road side soils, water, biota, and sediment samples not only in developed countries, but also in developing countries. Most of these studies which were done in the developed countries have demonstrated the existence of increasing concentration of PGM in roadside environments, presenting undoubtful evidence that the automobile catalytic converters are the predominant source of these heavy metal pollutants in the environment [1-5].

PGM in the environment have been linked to the emission of these metals used as active metal catalysts in internal combustion engines to reduce the emission of hydrocarbons, carbon

Maejo Int. J. Sci. Technol. **2011**, *5*(03), 331-349

monoxide and nitrogen oxides [3-5]. The total extent of the emission, its composition in terms of relative concentrations of these elements, and the average size of the emitted particles strongly depend on the catalytic converter type and the traffic condition, although the age of the catalytic converter may also in part be another factor [6]. Also, it was previously believed that the soluble fraction of the emitted PGM was low, but recent studies have demonstrated that this fraction has increased tremendously [7].

Ghana relies heavily on the import of used vehicles (5-12 years old), which may constitute about 70% of the vehicular fleet in this country [8]. This situation raises fears of possible deposition of PGM in the environment, which may end up in water bodies and soils (along the roadways). Also, studies on the Ghanaian environment have shown the presence of elevated levels of PGM in sediment and some biological species [9-10]. It is believed that in addition to the availability of PGM in terrestrial ecosystems, these metals are also introduced passively in aquatic biotopes by road run-off into lakes and rivers, where the metals accumulate in the sediment [11].

Although PGM are not yet considered a serious health risk, studies suggest that they can potentially pose danger in the future as worldwide car sales keep increasing [4]. The accumulation of Pd and Pt should be of great concern as they are known to have some mutagenic and toxic effects, even at very low concentrations [12]. PGM are known to have very good catalytic properties and therefore their presence in the environment may trigger several chemical and biochemical processes which may affect the environment. The chemistry of platinum compounds in aqueous solutions is dominated by the formation of complex compounds. Many of the salts of PGM, particularly those with halogen or nitrogen-donor ligands, are water-soluble. Platinum (as well as the other platinum group metals) has a pronounced tendency to react with carbon compounds such as alkenes and alkynes, forming Pt(II) coordination complexes [13].

Although Pt does not corrode in air, it can be affected by halogens, cyanides, sulphur and other heavy metals and hydroxides, which makes it mobile in the environment [14]. In soil, the mobility of platinum depends on the pH, redox potential, chloride concentration, and the chemical form of Pt in the primary rock. The soluble forms of the PGM are absorbed by plants, raising the possibility of its presence in the food chain [8].

This study was done to assess the levels, transport, distribution and source of PGM in water and sediment samples from seven water bodies along the coastal belt of Ghana.

MATERIALS AND METHODS

The study area lies between latitudes 5–6^{o}N and longitudes 1^{o}7'–1^{o}45'W as shown in Figure 1. The sites are: Pra estuary at Shama (western region), Benya lagoon at Elmina, Fosu lagoon in Cape Coast, Narkwa lagoon at Narkwa (all in the central region of Ghana), Sakumono 2 lagoon near Tema (Greater Accra), Volta estuary at Anyanuin and Keta lagoon (easternmost, both in the Volta region). Each of these water bodies plays a significant role as far as fishery activities are concerned in Ghana. Two sampling sites A and B, about 1 kilometre apart, were chosen at each study area where samples A and B were taken.

Maejo Int. J. Sci. Technol. **2011**, *5*(03), 331-349

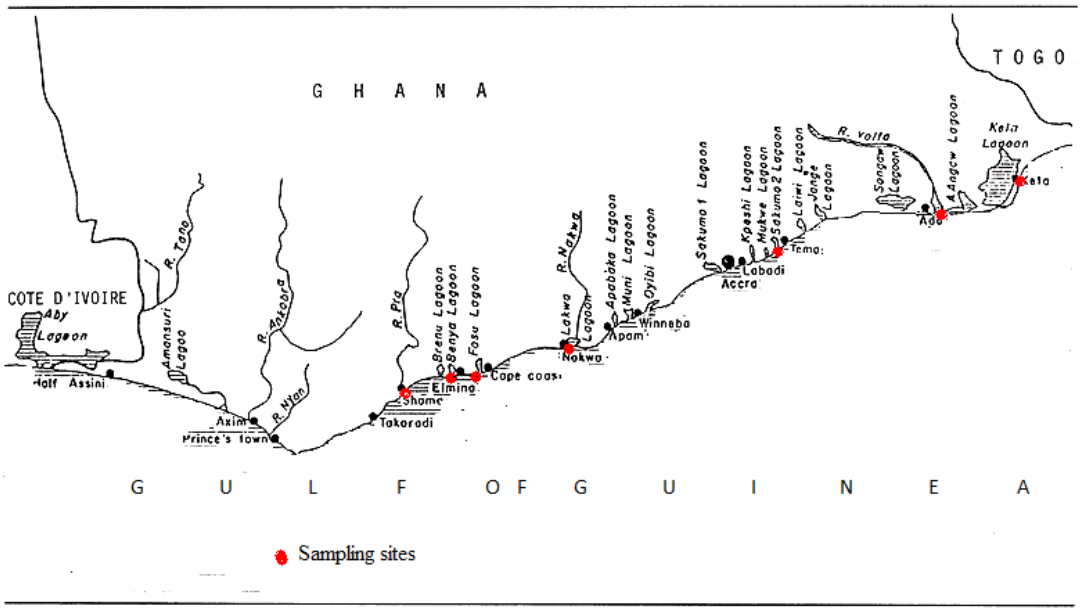

Figure 1. Map showing the sampling sites

Two sediment samples (riverbed soil), labelled A and B, were collected from the middle part of the river/lagoon (about 100 metres from the bank) at each site. Using a fishing boat, each sediment sample (about 200 g) was scooped into a black polyethylene container. Samples were further prepared for laboratory analysis by air drying at room temperature for three days.

Two water samples in 1-litre polyethylene bottles, labelled A and B, were also collected at the same sampling points where sediment A and B respectively were taken. The bottles were pre-washed with acetone to remove any grease, then with dilute nitric acid to dissolve any metal before rinsing with distilled water. The labelled sediment and water samples were kept in the refrigerator and later sent to the Ghana Atomic Energy Commission laboratory for neutron activation analysis (NAA) with a 30-kW miniature neutron source reactor supplied by the international atomic energy agency (IAEA).

The physicochemical variables determined for the water samples were pH, dissolved oxygen (DO), refractive index, salinity and turbidity. The DO was determined with an oxygen meter (model: AZ8403, A.W.R. Smith Process Instrumentation). The pH was measured using a bench-top pH meter (model AZ86555, Eztech Instruments). The pH meter was calibrated with pH tablets (pH 4 and 8). The refractive index was measured in the laboratory with an Abbe refractometer (model AR2008, A. Krüss Optronics). The salinity was measured on-site using an Abbe refractometer (model AR2008, A. Krüss Optronics) with an in-built salinity scale. The turbidity was determined on-site using a Micro1000 turbidimeter (model HFS-20014, Preiser Scientific). All measurements were done in duplicate and averaged.

For the INAA of the PGM, exactly 0.5 mL of each water sample was transferred using a calibrated Eppendorf-tip ejector pipette to a clean pre-weighed 1.5-mL rabbit capsule (sample vial),

Maejo Int. J. Sci. Technol. **2011**, *5*(03), 331-349

reweighed and heat-sealed. Four of these sample vials were packed into 7.0-mL rabbit capsule and heat-sealed for irradiation [15].

Each sediment sample was air-dried for 3 days in a clean environment and organic debris, shells, stones and some organisms physically removed. It was then crushed with an agate mortar and pestle, sieved through an 85-µm-mesh sieve and homogenised. About 100 mg was weighed onto a clean polyethylene film, which was then wrapped and heat-sealed. It was then packed into a 7-mL volume rabbit capsule and heat-sealed for irradiation. Certified reference material, SARM 7 (platinum ore), prepared by the National Institute for Metallurgy and distributed by South African Bureau of Standards Reference Materials, was treated the same way as the samples [15].

The determination of the trace PGM was done by NAA method using thermal neutron from a low-flux Am-Be radioisotope. Theoretically, NAA is based on the measurement of characteristic gamma-ray from radionuclei formed from a specific neutron reaction which can be used to measure the amount of the elements using the usual radioactive decay law [16-17]. The irradiation source was a 20-curie Am-Be radioactive neutron source and the thermal neutron flux at the irradiation site was 5.0×10^{11} $ns^{-1}cm^{-2}$. Each of the samples was sent by the pneumatic transfer system into the Am-Be source for a 1-hour irradiation and left overnight to cool or for decaying process to take place. The irradiated sample was placed on top of the detector and counts were accumulated for pre-selected time to obtain the spectral intensities. For short and medium irradiation, 600-second counting time was chosen and the intensities of the photo peaks recorded for further analysis.

Counting of signals was done by an ENERTEC high germanium (HPGe) detector of 3000 (+ve) bias with a resolution of 2.55 keV for 1332 KeV photo peak of Co-60. A Microsoft Windows-based software (MAESTRO) was used for qualitative and quantitative spectrum analyses [17-18]. Validation of the analytical procedure was undertaken by irradiating an IAEA standard reference material (SARM 7 platinum ore) and counting under identical experimental conditions. The analytical values of the reference material obtained from this study were compared with the recommended values (in ppm).

The pollution load index (PLI), contamination factor (CF) and geo-accumulation index (Igeo) were used to assess and quantify the levels of pollution of the monitored element in the sediment and water samples of the study areas [19-24]. The mean concentrations, standard deviations and correlation matrices for the sediment data were determined using SPSS version 16 software. According to Tomlinson et al. [19], the indices enable the quality of the environment to be easily understood by a non-specialist. The CF (= element concentration in soil / background value in the earth crust) was computed for the sediment using the average elemental concentration and the maximum corresponding value in the world-average abundance of metals in the earth crust (0.005, 0.005 and 0.0002 ppm for Pt, Pd and Rh respectively) [25-26].

The resultant CF values of the elements were used to compute the PLI as a measure of the mutual pollution effect on the soils [17, 19, 27]. In this case, $PLI = 3\sqrt{CF_{Pt} \times CF_{Pd} \times CF_{Rh}}$ (3=number of metals studied).

The Igeo approach was used to quantify the degree of anthropogenic contamination in soils with regard to the different elements monitored [22]. The Igeo for each element was calculated using the formula: $Igeo = \log 2 (Cn/1.5 \times Bn)$, where Cn is the measured element concentration in the soil

Maejo Int. J. Sci. Technol. **2011**, *5*(03), 331-349

(sediment) sample and Bn is the geochemical background value in a world-average shale, or the maximum corresponding value in the world-average abundance of the metal in the earth crust reported [25-26, 28].

For water samples, the contamination degree was used to assess an excessive contamination value of the monitored element. This was calculated using the expression: $CD = \sum Cfi$, where CD is the contamination degree and *Cfi* (the contamination factor for the i^{th} element) = (Cn/Cb)-1, where Cn is the analytical value of the i^{th} element and Cb is the upper permissible limit of the element in water [29].

In this study, guideline values for the dietary intake (0.20 µg/g/day for Pt and Rh, and 1.00 µg/g/day for Pd) [30-31] were selected for the calculation of the contamination degree of the water samples since it was difficult to get guideline values for drinking water.

RESULTS AND DISCUSSION

The accuracy and precision of the analytical technique (NAA) was measured by simultaneous activation of the certified reference material SARM 7 (platinum ore). Table 1 shows the analytical results obtained for the reference material compared with the standard concentration values. The values compare favourably well with the standard values for Pt, Pd and Rh with less than 6% bias. The precision was calculated as a per cent relative standard deviation (%RSD) of three replicated samples of the prepared standard, which were found to be less than 5% with recovery of about 98% (Table 1).

Table 1. Result of the quality control analysis of SARM 7

PGM	Standard concentration (SARM 7)	Results obtained after NAA analysis of the standards Std.1	Std. 2	Std. 3	Mean	Recovery (%)
Pt (µg/g)	3.74±0.045	3.65±0.55	3.70±0.56	3.71±0.56	3.69±0.56	98.6
Pd (µg/g)	1.53±0.032	1.49± 0.22	1.51±0.23	1.49±0.23	1.50±0.23	98.0
Rh (µg/g)	0.24±0.013	0.23± 0.04	0.22±0.033	0.20±0.04	0.23±0.04	96.95

The results of the analysis of the sediment samples (wet and dry season) showed the presence of the platinum group metals at all the seven sampling sites. The dry-season samples generally recorded higher PGM levels as shown in Appendix 1, which presents details of mean concentration at each sampling site (A and B). Table 2 presents mean PGM concentrations (mean of A and B (n = 2)) of the seven water bodies studied. The mean PGM values ranged between 0.0002 µg/g (Rh) and 0.095 µg/g (Pd) for sediment, and 0.001µg/L (Rh) and 0.019 µg/L (Pd) for water samples (Table 2). The Keta lagoon recorded the highest PGM mean concentrations for both sediment and water samples. The general trend of the distribution of PGM in the sediment followed a decreasing order of Keta > Narkwa > Benya > Pra > Fosu > Sakumono 2 > Volta estuary.

Maejo Int. J. Sci. Technol. **2011**, *5*(03), 331-349

Table 2. Mean concentrations of PGM in sediment and water samples of 7 water bodies along the coastal belt of Ghana

Sampling site	Mean PGM value		
	Pt	**Pd**	**Rh**
Sediment (µg/g)			
Pra estuary	0.034	0.052	0.0002
Benya lagoon	0.056	0.076	0.005
Fosu lagoon	0.032	0.027	0.001
Narkwa lagoon	0.054	0.073	0.003
Sakumono 2 lagoon	0.027	0.034	0.001
Volta estuary	0.007	0.024	0.003
Keta lagoon	0.047	0.095	0.010
Water (µg/L)			
Pra estuary	0.005	0.003	0.002
Benya lagoon	0.005	0.008	0.002
Fosu lagoon	0.004	0.013	0.002
Narkwa lagoon	0.004	0.009	0.001
Sakumono 2 lagoon	0.005	0.009	0.001
Volta estuary	0.012	0.017	0.002
Keta lagoon	0.011	0.019	0.002

The high concentrations of the metals recorded at Keta lagoon might be attributed to its direct contact with the sea and close proximity to highways with heavy traffic, resulting in a higher vehicular PGM deposition [11]. The situation was different at the Narkwa lagoon where even though there was not much vehicular activities close to the lagoon, yet it recorded elevated mean values of PGM (0.001–0.073 µg/g) for the sediment. In this case, there was an extensive use of outboard motors and some marine vessels, which might have contributed to the elevated PGM [32-33]. Sites which are far away from the sea but close to highways (Volta Lake, River Pra estuary and Benya lagoon in Elmina) also recorded appreciable levels of PGM. A study in Ghana by Essumang et al. [8] also reported similar elevated PGM results.

Palladium metal recorded the highest concentrations and rhodium the lowest. This trend was also observed by Essumang et al. [8-9] in their PGM study on the Pra River estuary. Thus, Pd seems to be the most distributed PGM with a distribution gradient of Pd ≥ Pt > Rh. Other studies have reported similar results which showed a higher proportion of Pd, which matched the recent change in the composition of the metal mixtures in catalytic converters used in automobile exhaust purification [11, 34]. The proportion of Pd in the catalyst has increased to approximately 96%, showing a dominant use of Pd in catalytic converters in recent years [35-36]. In addition, palladium in the biosphere can exist in metallic or oxide forms which are sparingly soluble in water, resistant to most reactions in the biosphere (e.g. abiotic degradation, UV-initiated reactions and oxidation by hydroxyl radicals) and do not volatilise [37], thus resulting in their greater accumulation in soil. The levels of

Maejo Int. J. Sci. Technol. **2011**, *5*(03), 331-349

all the examined metals in the riverine sediment and water column might result in the reduction in the benthic biodiversity [4, 22].

Table 3 shows the physicochemical properties of the water samples from the seven sampling sites. The DO values in various water bodies did not show significant difference between the seasons. The values indicated moderate DO content, attributable to the build-up of organic waste in the lagoons. There was also no significant difference in the pH and refractive index values of the water bodies. The pH values were mostly on the slightly basic side and that might have contributed to the very low PGM values in the water column as a basic medium does not support metal dissolution.

High values of pH: 8.37, 8.12 and 8.80 were recorded in the dry season at Sakumono 2, Narkwa and Keta respectively. This situation should be due to the fact that these lagoons are the 'open' types and always open to the ocean where the average pH of sea water is 8.2 [38] Similar high pH has been reported for a lagoon open to the ocean and filled with a high population of algae [38]. In the case of salinity, significant differences were observed as a result of influx from the ocean for some sites. Turbidity values were slightly higher during the rainy season for some sites while lower for others. This could be attributed to the diurnal variations and different environmental pollution state of these water bodies.

Table 3. Summary of average physicochemical properties studied in rainy and dry seasons in various coastal water bodies

Physicochemical property	Pra	Benya	Fosu	Narkwa	Sakumono 2	Volta	Keta
DO (%)							
Dry season	8.90	6.30	7.50	7.14	7.60	6.20	7.60
Wet season	7.79	7.28	7.38	7.38	7.55	6.75	7.50
Mean	8.35	6.79	7.44	7.26	7.58	6.48	7.55
pH							
Dry season	7.67	7.33	7.12	8.37	8.12	7.93	8.80
Wet season	6.15	7.54	8.15	7.54	7.21	7.25	7.74
Mean	6.91	7.44	7.64	7.96	7.67	7.59	8.27
Refractive index							
Dry season	1.332	1.336	1.335	1.338	1.336	1.334	1.336
Wet season	1.333	1.338	1.335	1.338	1.334	1.334	1.337
Mean	1.333	1.337	1.338	1.338	1.335	1.334	1.337
Salinity (%)							
Dry season	0.00	27.70	0.50	25.50	2.80	1.50	2.00
Wet season	0.00	26.80	9.30	27.00	6.50	10.50	21.00
Mean	0.00	27.25	4.90	26.25	4.65	6.00	11.50
Turbidity (ppm)							
Dry season	36.50	26.00	66.30	31.80	46.50	29.80	10.30
Wet season	52.00	48.80	43.80	29.00	50.50	23.00	22.30
Mean	44.25	37.40	55.05	30.40	48.50	26.40	16.30

Maejo Int. J. Sci. Technol. **2011**, *5*(03), 331-349

CF, PLI and Igeo for sediment and water samples are presented in Table 4. Keta lagoon sediment had the highest CF values for Pd and Pt (35.40 and 34.96 respectively) in the dry season, followed by Sukumono 2 lagoon with Pd CF value of 28.96 in the wet season. Pra estuary, Narkwa lagoon and Benya lagoon recorded CF values of 20.08, 27.56 and 21.48 respectively for Pd and Pt, which were all less than 100 (Table 4).

Table 4. Contamination factor (CF), pollution load index (PLI) and geo-accumulation index (Igeo) of PGM in sediment and water

Sediment	Season	CF(Pt)	CF(Pd)	CF(Rh)	PLI	Igeo(Pt)	Igeo(Pd)	Igeo(Rh)
Pra Estuary								
A	Dry	7.88	13.48	0.48	3.71	1.58	2.71	0.00
	Wet	0.00	6.92	0.08	0.74	0.00	1.39	2.40
B	Dry	8.96	20.08	0.04	1.93	1.79	4.03	0.20
	Wet	2.20	1.24	0.04	0.48	0.44	0.25	0.20
Benya lagoon								
A	Dry	0.00	16.2	0.24	1.97	0.00	3.25	1.20
	Wet	0.00	16.4	0.16	1.62	0.00	3.29	0.80
B	Dry	7.56	21.48	1.56	0.33	1.52	4.31	7.83
	Wet	14.68	5.92	0.00	9.32	2.95	1.18	0.00
Fosu lagoon								
A	Dry	3.48	2.04	0.00	1.12	0.69	0.41	0.00
	Wet	1.48	16.52	0.20	1.69	0.29	3.32	1.00
B	Dry	2.04	1.28	0.04	0.47	0.41	0.26	0.20
	Wet	18.68	0.00	0.00	0.91	3.75	0.00	0.00
Narkwa lagoon								
A	Dry	27.56	13.68	1.96	9.04	5.53	2.74	9.83
	Wet	3.32	4.80	0.16	1.37	0.67	0.96	0.80
B	Dry	0.16	15.16	0.08	0.58	0.03	3.04	0.40
	Wet	11.36	24.36	0.00	16.64	2.28	4.89	0.40
Sakumono 2 lagoon								
A	Dry	5.56	8.32	0.00	6.80	1.12	1.67	0.00
	Wet	0.00	4.08	0.12	0.69	0.00	0.82	0.60
B	Dry	4.68	6.52	0.24	1.94	0.94	1.31	1.20
	Wet	0.00	28.96	0.16	2.15	0.00	5.81	0.80
Volta estuary								
A	Dry	0.96	2.88	0.08	0.60	0.19	0.58	0.40
	Wet	0.00	0.00	0.02	0.09	0.00	0.00	0.08
B	Dry	3.24	3.88	0.00	3.55	0.65	0.78	0.00
	Wet	5.56	9.32	0.04	1.28	1.12	1.87	0.20
Keta lagoon								
A	Dry	34.96	35.40	1.48	12.24	7.02	7.10	7.43
	Wet	2.32	6.92	0.04	0.86	0.47	1.39	0.20
B	Dry	0.00	21.44	0.88	4.34	0.00	4.30	4.41
	Wet	0.00	11.56	0.00	0.77	0.00	2.32	0.00

Maejo Int. J. Sci. Technol. **2011**, *5*(03), 331-349

Table 4. (Continued)

Water	Season	CF(Pt)	CF(Pd)	CF(Rh)	PLI	Igeo(Pt)	Igeo(Pd)	Igeo(Rh)
Pra estuary								
A	Dry	1.36	0.36	0.20	0.46	-1.45	-1.58	-1.56
	Wet	0.32	0.40	0.32	0.46			
B	Dry	1.52	1.04	0.32	0.79			
	Wet	0.44	0.36	0.12	0.27			
Benya lagoon								
A	Dry	1.28	3.04	0.68	1.38	-1.42	-1.54	-1.55
	Wet	0.28	0.36	0.24	0.29			
B	Dry	1.96	1.72	0.16	0.81			
	Wet	0.16	0.76	0.08	0.21			
Fosu lagoon								
A	Dry	0.00	4.20	0.68	1.69	-1.53	-1.49	-1.56
	Wet	0.08	3.76	0.08	0.29			
B	Dry	2.48	1.88	0.12	0.82			
	Wet	0.12	0.44	0.00	0.23			
Narkwa lagoon								
A	Dry	0.92	3.88	0.00	1.89	-1.47	-1.53	-1.58
	Wet	0.28	1.44	0.00	0.64			
B	Dry	1.84	1.96	0.36	1.09			
	Wet	0.48	0.00	0.00	0.27			
Sakumono 2 lagoon								
A	Dry	0.40	1.48	0.40	0.62	-1.42	-1.54	-1.56
	Wet	0.16	0.32	0.16	0.20			
B	Dry	3.00	4.08	0.16	1.25			
	Wet	0.16	0.64	0.04	0.16			
Volta estuary								
A	Dry	3.44	3.72	0.00	3.58	-1.01	-1.49	-1.59
	Wet	1.12	1.68	0.00	1.37			
B	Dry	3.00	4.08	0.14	1.19			
	Wet	1.12	3.76	0.12	0.79			
Keta lagoon								
A	Dry	3.24	3.68	0.00	3.45	-1.23	-1.49	-1.56
	Wet	1.52	1.60	0.32	0.92			
B	Dry	2.44	4.00	0.40	1.58			
	Wet	0.24	1.20	0.08	0.29			

Note: A and B are two sampling sites at each water body under study.

Maejo Int. J. Sci. Technol. **2011**, *5*(03), 331-349

The CF assessment of the quality of sediment of the lagoons studied indicated contamination mainly with Pt and Pd. It also showed that Rh did not seem to contaminate the sediment in any of the sites. CF values of Pt and Pd were generally greater than 3, indicating high contamination in the sediment at most sampling sites. This result is not surprising since most of the sites are close to highways except Volta and Narkwa lagoons. However, the rivers of these estuaries (Volta and Narkwa) go through several urban communities, thereby carrying some PGM to the sediment.

The CF values of water samples were generally lower than those of the sediment with Pt and Pd contributing to moderate pollution in the water bodies. Most of the Pt and Pd CF values recorded were slightly above 3 except for the Pra estuary. In the case of Rh, all the sampling sites recorded CF values of less than 3, indicating no pollution of the water bodies by Rh.

The PLI values of the sediment and water from all the studied sites were between 0.09–16.64, with the highest value of 16.64 at Narkwa lagoon, followed by Keta lagoon (12.24) and Benya lagoon (9.32), while the range for water samples was 0.16–3.58. Several sediment and water samples had PLI values greater than 1, demonstrating progressive deterioration of the environment by PGM. Also, most samples with PLI values greater than 1 were collected in the dry season. These values indicate that Pra, Benya, Narkwa, Sakumono and Keta sites underwent progressive environmental deterioration while Fosu lagoon and Volta estuary showed baseline levels of PGM pollutants in sediment. In the case of water samples, Pra, Benya, Fosu Narkwa and Sakumono 2 showed baseline levels of pollutants present while Keta and Volta estuary sites showed some degree of progressive deterioration of the water bodies [19–21].

The Igeo values in sediment ranged between 0.00–7.02 for Pt, 0.00–7.10 for Pd, and 0.00-9.83 for Rh. The two highest Igeo values of 9.83 and 7.83 (Rh) were recorded at Narkwa and Benya lagoons respectively for dry season samples. Overall, the Igeo values for Pd were the highest followed by Pt and Rh from site-to-site comparison (Table 4). These values for the sediment samples indicate that the presence of PGM in the environment was probably from anthropogenic sources. The values varied across the sampling sites and indicated moderate to strong pollution situations. Most of the values were less than 5, above which a situation of very high pollution is indicated [39]. Sites which registered values greater than 5 for sediment samples were Benya lagoon (Rh), Narkwa lagoon (Pt and Rh) and Keta lagoon (Pt, Pd and Rh).

For water samples, however, CD was used to assess the pollution status of the water bodies. The CD for all the elements recorded values less than 1, signifying low pollution of the metals in the water columns at the sampling sites [29].

The correlation matrices of the elements from the sampling sites demonstrated good positive interrelationships between the three elements studied. These elements showed correlation at 0.01 level (99%), suggesting their common source in the studied areas [17]. However, there was no correlation between the PGM in the water columns and those in the sediments (Table 5), indicating that the accumulation of these elements in the sediment might not depend on the amount received by the water column. This therefore suggests that there was another source influencing the distribution of the metals between water and sediment. However, it was also possible that such environmental factors as water current and pH contributed to such situation. Only one positive correlation between Pt and Rh in the sediment and water (0.637) at 0.05 level was observed. This demonstrates that the

Maejo Int. J. Sci. Technol. **2011**, *5*(03), 331-349

distribution of the metals in the water and sediment could be altered by environmental factors such as geological area or soil type, acidity and alkalinity. The metal-to-metal relationships at all the sampling sites seem to correlate perfectly at 0.01 level as expected for the metals in both sediment and water.

Table 5. Pearson correlation between elements in water and sediment

Element	Pt (water)	Pd (water)	Rh (water)	Pt (sed.)	Pd (sed.)	Rh (sed.)
Pt (water)	1					
Pd (water)	0.256	1				
Rh (water)	-0.448	0.071	1			
Pt (sediment)	0.129	-0.139	-0.129	1		
Pd (sediment)	0.135	0.06	0.202	0.357	1	
Rh (sediment)	0.001	0.031	-0.341	0.637*	0.453	1

* Correlation is significant at the 0.05 level.

The interrelationships among the PGM in sediment and water at each sampling site were also investigated (Table 6). The elements showed positive significant correlation from site to site at both 0.01 and 0.05 levels. Platinum from Benya lagoon showed a strong correlation (1.00) at 0.01 level with platinum and palladium at Keta lagoon as well as palladium from Pra River estuary and Sakumono 2 lagoon. Palladium from Benya lagoon correlated well with that of Keta lagoon and Pra River estuary at 0.998 and 0.985 respectively. At 0.05 level, another strong positive correlation ranging between 0.990-0.999 was also observed between platinum at Pra, Fosu, Benya and Narkwa lagoons as well as Volta estuary. In addition, palladium to platinum and rhodium correlations were also recorded at the same range and level (Table 6). The general strong correlations between PGM concentrations in the study areas suggest a common anthropogenic source, most likely automobile emissions, of these elements.

It was also observed from the Pearson's correlation analysis that rhodium at Pra estuary correlated negatively with platinum at Benya, Fosu and Volta, palladium at Sakumono 2 and Volta, and Rh at Benya, with values ranging between 0.9270–0.990 at 0.05 level (Table 6). Platinum concentration at Benya also recorded a negative correlation with Pd at Narkwa and Benya, which suggested another possible source of PGM. A possible source of Rh other than vehicular emissions was gold mine waste discharged into Pra River as rhodium has been found to be associated with gold ore [40]. This situation was possible as Ghana is covered by the Paleoprotoerozoic rocks of the Birimian Super group and the overlying clastic sedimentary [41]. Placer gold deposits, also referred to as 'alluvial gold', were found in the stretch of the Pra River, in which Rh occurred as a by-product. Also, PGM may occur naturally in the alluvial sand [42]. All these water bodies deposit their debris into the Gulf of Guinea, hence the possibility of contributing to Rh level in the Pra River estuary. The correlation coefficients for the PGM in sediment and water in the study areas suggest

Maejo Int. J. Sci. Technol. **2011**, *5*(03), 331-349

Table 6. Pearson correlation matrix of PGM in samples from each site

	Pra Pt	By Pt	Fs Pt	Nk Pt	Sak Pt	Vt Pt	Kt Pt	Pra Pd	By Pd	Fs Pd	Nk Pd	Sak Pd	Vt Pd	Kt Pd	Pra Rh	By Rh	Fs Rh	Nk Rh	Sak Rh	Vt Rh	Kt Rh
Pra Pt	1.000																				
By Pt	0.999*	1.000																			
Fs Pt	0.503	0.997*	1.000																		
Nk Pt	0.943*	0.997*	0.186	1.000																	
Sak Pt	0.864	0.990*	0.866	0.650	1.000																
Vt Pt	-0.074	0.994*	0.815	-0.400	0.419	1.000															
Kt Pt	0.781	1.00**	-0.245	0.960	0.301	-0.759	1.000														
Pra Pd	0.953*	1.00**	0.738	0.790	0.969*	0.233	0.509	1.000													
By Pd	0.988**	0.998*	0.609	0.890	0.913*	0.069	0.676	0.99**	1.000												
Fs Pd	0.615	-0.491	-0.335	0.820	0.143	-0.740	0.926	0.377	0.532	1.000											
Nk Pd	0.680	0 .998*	0.965*	0.396	0.937*	0.683	-0.081	0.869	0.776	-0.085	1.000										
Sak Pd	0.510	1.00**	0.998**	0.194	0.866	0.817	-0.261	0.746	0.621	-0.311	0 .973*	1.000									
Vt Pd	0.224	0.961	0.942*	-0.110	0.683	0.904*	-0.422	0.492	0.332	-0.621	0.821	0.928*	1.000								
Kt Pd	0 .996**	1.00**	0.560	0.915*	0.891	0.000	0.730	0.972*	0.99**	0.576	0.733	0.571	0.280	1.000							
Pra Rh	-0.260	-0.992*	-0.965*	0.075	-0.708	-.927*	0.455	-0.535	-0.380	0.568	-0.868	-0.959*	-0.99**	-0.323	1.000						
By Rh	0.248	0.964	0.914*	-0.076	0.649	.931*	-0.62	0.527	0.392	-0.443	0.872	0.928*	0.877	0.328	-0.934*	1.000					
Fs Rh	-0.424	-0.692	-0.747	-0.209	-0.717	-0.477	-0.115	-0.554	-0.443	0.370	-0.640	-0.708	-0.799	-0.428	0.729	-0.453	1.000				
Nk Rh	0.557	-1.00**	-0.629	0.828	-0.085	-0.902	1.00**	0.205	0.399	0.959	-0.370	-0.598	-0.879	0.472	0.816	-0.681	0.969	1.000			
Sak Rh	0.220	0.974	0.917*	-0.108	0.638	0.946*	-0.623	0.504	0.364	-0.486	0.860	0.929*	0.897	0.300	-0.948*	0.99**	-0.48	-0.720	1.000		
Vt Rh	-0.908	-1.00**	-0.669	-0.684	0.971	-0.286	1.00**	-0.99*	-0.968	-0.431	-0.860	-0.697	-0.334	-0.945	0.442	-0.616	0.091	-0.157	-0.577	1.000	
Kt Rh	0.898	0.990*	0.796	0.711	0.963*	0.354	0.362	0.98**	0.955*	0.304	0.922*	0.810	0.552	0.933*	-0.611	0.647	-0.500	0.070	0.620	-0.990*	1.000

* Correlation is significant at the 0.05 level

** Correlation is significant at the 0.01 level

Note: PraPt = Pra Platinum, ByPt = Benya Platinum, FSPt = Fosu Platinum, NkPt = Narkwa Platinum, SakPt = Sakumono 2 Platinum, VtPt = Volta Platinum and KtPt = Keta Platinum
PraPd = Pra Palladium, ByPd = Benya Palladium, FsPd = Fosu Palladium, NkPd = Narkwa Palladium, SakPd= Sakumono 2 Palladium, VtPdt = Volta Palladium and KtPd= Keta Palladium
PraRh = Pra Rhodium, ByRh = Benya Rhodium, FsRh = Fosu Rhodium, NkRh = Narkwa Rhodium, SakRh = Sakumono 2 Rhodium, VtRh= Volta Rhodium, and KtRh = Keta Rhodium

Maejo Int. J. Sci. Technol. **2011**, *5*(03), 331-349

both strong negative and positive correlations within the sampling sites, implying that sources other than vehicular emissions, such as hospital effluent and gold mining activities might also contribute. The effect of gold mining operations should be investigated further to ascertain its influence on environmental PGM.

CONCLUSIONS

This study shows that there was moderate to high platinum-group-metal contamination along the coast of Ghana, which was most likely attributed to anthropogenic activities. The degree of contamination among the three metals was generally in the order: Pd > Pd > Rh, the most mobile element being Pd. The study suggests a distribution gradient: Pd ≥ Pt > Rh. The pollution indices showed moderate to high contamination at all the study sites in the case of sediment while there was less pollution of water. The study has provided useful information on the water quality status of some of our lagoons and estuaries along the coastal belt and may serve as a reference for future research studies.

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Maejo Int. J. Sci. Technol. **2011**, *5*(03), 331-349

APPENDIX 1. PGM mean concentration in sediment and water samples at sampling sites A and B along the coastal belt of Ghana

Sampling site		Season	Mean PGM		
			Pt	**Pd**	**Rh**
Pra estuary					
	A	Dry	0.039±0.006	0.067±0.010	0.002±0.000
		Wet	nd	0.035±0.005	0.0004±0.001
Sediment (µg/g)		**Mean**	**0.039±0.006**	**0.051**	**0.0012**
		SD	**0.000**	**0.023**	**0.001**
	B	Dry	0.0448±0.007	0.100±0.000	0.0002±0.000
		Wet	0.011±0.002	0.006±0.015	0.0002±0.000
		Mean	**0.028**	**0.053**	**0.0002±0.000**
		SD	**0.024**	**0.066**	**0.000**
	A	Dry	0.007±0.001	0.002±0.000	0.001±0.000
		Wet	0.002±0.000	0.002±0.000	0.002±0.000
Water (µg/L)		**Mean**	**0.005**	**0.002**	**0.0015**
		SD	**0.004**	**0.000**	**0.001**
	B	Dry	0.008±0.001	0.005±0.001	0.002±0.000
		Wet	0.002±0.000	0.002±0.000	0.001±0.000
		Mean	**0.005**	**0.004**	**0.002**
		SD	**0.004**	**0.002**	**0.001**
Benya lagoon					
	A	Dry	nd	0.081±0.012	0.001±0.000
		Wet	nd	0.082±0.012	0.001±0.000
Sediment (µg/g)		**Mean**	**nd**	**0.082**	**0.001±0.000**
		SD	**0.000**	**0.001**	**0.000**
	B	Dry	0.038±0.001	0.107±0.016	0.008±0.001
		Wet	0.073±0.011	0.030±0.004	nd
		Mean	**0.056**	**0.069**	**0.008±0.001**
		SD	**0.025**	**0.054**	**0.000**
	A	Dry	0.006±0.001	0.015±0.002	0.003±0.001
		Wet	0.001±0.000	0.002±0.000	0.001±0.000
Water (µg/L)		**Mean**	**0.004**	**0.009**	**0.002**
		SD	**0.004**	**0.009**	**0.001**
	B	Dry	0.010±0.000	0.009±0.001	0.001±0.000
		Wet	0.001±0.000	0.004±0.001	0.0004±0.000
		Mean	**0.006**	**0.007**	**0.001**
		SD	**0.006**	**0.004**	**0.0004**
Fosu lagoon					
	A	Dry	0.017±0.003	0.010±0.002	nd
		Wet	0.007±0.001	0.083±0.012	0.001±0.000
Sediment (µg/g)		**Mean**	**0.012**	**0.047**	**0.001±0.000**
		SD	**0.007**	**0.052**	**0.00**
	B	Dry	0.010±0.002	0.006±0.01	0.0002±0.000
		Wet	0.093±0.014	nd	nd
		Mean	**0.052**	**0.006**	**0.0002**
		SD	**0.059**	**0.000**	**0.00**
	A	Dry	nd	0.021±0.003	0.003±0.000
		Wet	0.0004±0.000	0.019±0.003	0.0004±0.000
Water (µg/L)		**Mean**	**0.0004**	**0.020**	**0.002**
		SD	**0.000**	**0.001**	**0.002**
	B	Dry	0.012±0.002	0.009±0.001	0.001±0.000
		Wet	0.001±0.000	0.002±0.000	nd
		Mean	**0.007**	**0.006**	**0.001±0.000**
		SD	**0.008**	**0.005**	**0.000**

Maejo Int. J. Sci. Technol. **2011**, *5*(03), 331-349

Sampling site		Season		Mean PGM	
Narkwa lagoon					
	A	Dry	0.139±0.021	0.068±0.010	0.010±0.001
		Wet	0.017±0.002	0.024±0.004	0.001±0.000
Sediment (µg/g)		**Mean**	**0.078**	**0.046**	**0.006**
		SD	**0.086**	**0.031**	**0.006**
	B	Dry	0.001±0.000	0.076±0.011	0.0004±0.000
		Wet	0.057±0.009	0.122±0.015	nd
		Mean	**0.029**	**0.099**	**0.0004**
		SD	**0.039**	**0.033**	**0.000**
	A	Dry	0.001±0.000	0.007±0.001	nd
		Wet	0.001±0.000	0.007±0.001	nd
Water (µg/L)		**Mean**	**0.001**	**0.007**	**nd**
		SD	**0.000**	**0.000**	**-**
	B	Dry	0.009±0.001	0.010±0.002	0.002±0.000
		Wet	0.002±0.000	nd	nd
		Mean	**0.006**	**0.010**	**0.002**
		SD	**0.005**	**0.000**	**0.000**
Sakumono 2 lagoon					
	A	Dry	0.028±0.004	0.042±0.006	nd
		Wet	nd	0.020±0.003	0.001±0.000
Sediment (µg/g)		**Mean**	**0.028**	**0.031**	**0.001**
		SD	**0.000**	**0.016**	**0.000**
	B	Dry	0.023±0.004	0.033±0.005	0.001±0.000
		Wet	0.028±0.004	0.042±0.006	nd
		Mean	**0.026**	**0.038**	**0.001**
		SD	**0.004**	**0.006**	**0.000**
	A	Dry	0.002±0.000	0.007±0.001	0.002±0.000
		Wet	0.001±0.000	0.002±0.000	0.001±0.000
Water (µg/L)		**Mean**	**0.002**	**0.005**	**0.0015**
		SD	**0.001**	**0.004**	**0.001**
	B	Dry	0.015±0.003	0.020±0.002	0.001±0.000
		Wet	0.001±0.000	0.003±0.001	0.0002±0.000
		Mean	**0.008**	**0.012**	**0.001**
		SD	**0.009**	**0.012**	**0.001**
Volta estuary					
	A	Dry	0.005±0.001	0.014±0.002	0.001±0.000
		Wet	nd	nd	nd
Sediment (µg/g)		**Mean**	**0.005**	**0.014**	**0.001**
		SD	**0.00**	**0.00**	**0.000**
	B	Dry	0.016±0.002	0.019±0.003	0.003±0.000
		Wet	0.028±0.004	0.047±0.007	0.006±0.001
		Mean	**0.022**	**0.033**	**0.0045**
		SD	**0.008**	**0.019**	**0.002**
	A	Dry	0.017±0.003	0.019±0.003	0.003±0.000
		Wet	0.006±0.001	0.008±0.001	0.001±0.000
Water (µg/L)		**Mean**	**0.012**	**0.014**	**0.002**
		SD	**0.008**	**0.008**	**0.001**
	B	Dry	0.015±0.002	0.020±0.003	0.003±0.000
		Wet	0.006±0.001	0.019±0.003	0.001±0.000
		Mean	**0.011**	**0.020**	**0.002**
		SD	**0.006**	**0.001**	

Maejo Int. J. Sci. Technol. **2011**, *5*(03), 331-349

Sampling site		Season		Mean PGM	
Keta lagoon					
	A	Dry	0.175±0.026	0.177±0.027	0.035±0.004
		Wet	0.012±0.002	0.035±0.003	0.0002±0.000
Sediment (μg/g)		**Mean**	**0.094**	**0.106**	**0.015**
		SD	**0.115**	**0.100**	**0.025**
	B	Dry	nd	0.107±0.016	0.004±0.001
		Wet	nd	0.058±0.001	nd
		Mean	**nd**	**0.083**	**0.004**
		SD	**-**	**0.035**	**0.00**
	A	Dry	0.016±0.002	0.018±0.003	0.003±0.000
		Wet	0.008±0.001	0.008±0.001	0.002±0.000
Water (μg/L)		**Mean**	**0.012**	**0.013**	**0.0025**
		SD	**0.006**	**0.007**	**0.001**
	B	Dry	0.012±0.002	0.020±0.002	0.002±0.000
		Wet	0.006±0.001	0.030±0.005	0.002±0.000
		Mean	**0.009**	**0.025**	**0.002**
		SD	**0.004**	**0.007**	**0.000**

Note: nd = not detected